SCIENCE FOR CERAMIC PRODUCTION

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CORUNDUM CERAMICS WITH A EUTECTIC ZINC-BEARING ADDITIVE

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The sintering specifics of ceramics based on aluminum oxide with a eutectic zinc-containing additive are investigated. It is established that introduction of 1% sintering additive in the GLMK alumina makes it possible at 1450°C to obtain ceramics with zero open porosity, a mean density of 3.84 g/cm^3, and a bending strength of 310 ± 40 MPa. This ceramics has a sealed porosity of around 1% and an average size of corundum crystals equal to 5 – 8 μm.

Corundum ceramics belong to the most widely applied contemporary materials due to their unique combination of properties, i.e., high mechanical strength, hardness, wear resistance, refractoriness, thermal conductivity, chemical resistance, and good insulating properties.

Numerous high-quality materials based on Al_2O_3 have been developed for electronics and electric engineering and for construction: VK-94-1, VK-94-2, A-94T, VK-95-1, VK-98-1, VK-100-1, 795, 799, TsM-332, kartinite, lukalox, sinoxal, minalund, sicor, koral-2, and other materials that are industrially produced or have passed industrial testing.

All the specified ceramic materials contain modifying additives. It is established that oxide materials without such additives have a low level of service properties, a poorly controlled microstructure, and a low density. [1].

Additives that form a liquid phase in sintering are at present mainly selected on the basis of accumulated experience; however, there are reports on theoretical approaches to this selection [2].

In analyzing the suitability of a particular additive for producing ceramics with a decreased sintering temperature, the authors in [3] propose to take into account such factors as the structure and type of the emerging liquid phase (the acid-base properties of the melt), the temperature of its emergence, the energy of the cation – modifier – oxygen bond in a multicomponent melt, and the geometry and electrostatic state of the surface separating the solid and the liquid phases. Based on these principles and taking into account the accumulated data of making ceramics based on aluminum oxide with a decreased sintering temperature, a series of eutectic systems was selected, whose introduction into corundum makes it possible to produce dense ceramics under lower firing temperatures (1300 – 1550°C). These ceramics have a high density, a fine-crystalline structure, and sufficiently high mechanical strength. Additives of these types, as well as the properties of ceramics containing these additives, are described in [3].

An analysis of the mentioned systems [3] suggests that in all cases SiO_2 is the component ensuring the acid nature of the melt. However, it is known that TiO_2 is one of the oxides providing for an acid state of the melt required for active dissolution of corundum and its subsequent precipitation [4]. Additives containing titanium dioxide are commonly used in the technology of corundum ceramics [5]. However, a eutectic containing zinc oxide is an additive of this group that has not been used earlier.

The purpose of our study was to analyze the regularities of sintering of corundum ceramics with a zinc-containing eutectic additive.

The initial material was GLMK alumina, which was first crushed by wet grinding to a particle size of 2 – 4 μm and only then was the previously prepared disperse powder of the additive introduced. The samples (bars 40 × 4 × 4 mm) were compressed at a pressure of 100 MPa and polyvinyl chloride in the amount of 1% of dry material was added as a temporary technological binder. Firing was carried out in an air medium within a temperature interval of 1300 – 1500°C with spacing of 50°C. Exposure at the final firing temperature in each case lasted 3 h. The compositions used in the experiments contained 0.5, 0.8, 1.0, 2.0, 3.0, and 4.0% additive of a eutectic composition. The sintering parameters and the mechanical strength of samples with different amounts of additive under a firing temperature of 1450°C are listed in Table 1.

It can be seen that as the amount of additive grows from 0.5 to 1.0%, the average density and three-point bending strength increases and the open porosity decreases. As the additive content increases from 1.0 to 4.0%, the average den-

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TABLE 1

Amount of additive, %	Properties of samples		
	mean density, g/cm^3	open porosity, %	three-point bending strength, MPa
0.5	3.03	23.9	120 ± 38
0.8	3.34	16.1	190 ± 35
1.0	3.84	0.0	310 ± 40
2.0	3.79	0.6	275 ± 42
3.0	3.70	1.2	240 ± 38
4.0	3.67	2.6	235 ± 35

TABLE 2

Firing temperature, °C	Properties of samples		
	mean density, g/cm^3	open porosity, %	three-point bending strength, MPa
1300	3.05	24.1	190 ± 35
1350	3.18	19.0	215 ± 42
1400	3.48	15.9	230 ± 35
1450	3.84	0.0	310 ± 40
1500	3.88	0.0	325 ± 38

sity and mechanical strength decrease, and the open porosity insignificantly increases. This apparently anomalous variations of the open porosity is related to the formation of aluminum titanate along the corundum crystal boundaries when more than 1% eutectic additive is introduced, which is corroborated by petrography analysis. It should be noted that the quantity of the titanate phase grows in proportion to increasing content of the sintering additives. A high anisotropy of the $Al_2O_3 \cdot TiO_2$ phase results in intense microcracking along the corundum crystal boundaries, and the growth of aluminum titanate crystals impedes the sintering of the sample.

The decrease in the average density and mechanical strength with the additive content increasing from 1 to 4% is related to the increasing open porosity and emerging sealed porosity in the material. When 1% additive is added, no sealed porosity is observed, the sealed porosity of the ceramic containing 2% additive is 1 – 2%, and the porosity of the sample with 4% additive is equal to 3 – 4%.

The effect of the firing temperature on the properties of ceramics was studied on samples containing 1% sintering additive. The firing temperature varied from 1300 to 1500°C with an internal of 50°C (Table 2). It can be seen from the above data that as the firing temperature increases, the average density and mechanical strength regularly increase and the sealed porosity decreases. It is possible to obtain dense ceramics at a temperature of 1450°C.

The regularities of ceramics containing 1% additive of the eutectic composition were studied as well. The non-isothermic sintering method was used to calculate the apparent activation energy [6]. The study results are shown in Fig. 1. It can be seen that sintering of ceramics occurs in two stages: the activation energy E_1 of the first stage is

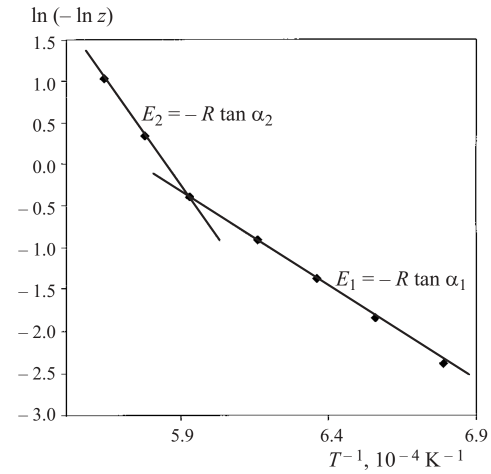

Fig. 1. Determination of apparent activation energy by the method of non-isothermic sintering [z) relative shrinkage, T) absolute temperature].

220 kJ/mole and that of the second stage E_2 is 330 kJ/mole. The change in sintering mechanism is observed at a temperature of about 1400°C, which is close to the melting temperature of the eutectic composition.

Consequently, sintering starts with regrouping of particles occurring at an early stage in the solid phase, which becomes possible at relatively low temperatures, since the material used is finely dispersed and active in sintering. At the second stage, sintering is controlled by the emerging eutectic melt. Apparently, the main mechanism determining the sintering process in this case is the dissolution of the high-melting phase and its subsequent precipitation.

Thus, introduction of a eutectic zinc-bearing additive in the amount of 1% into GLMK alumina produces a ceramic material with a sintering temperature of 1450°C, zero open porosity, mean density of 3.84 g/cm^3, and bending strength of 310 ± 40 MPa. The ceramic has a sealed porosity around 1% and the mean size of the corundum crystals is equal to 5 – 8 μm.

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